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Salt-solvent synchro-constructed robust electrolyte-electrode interphase for high-voltage lithium metal batteries

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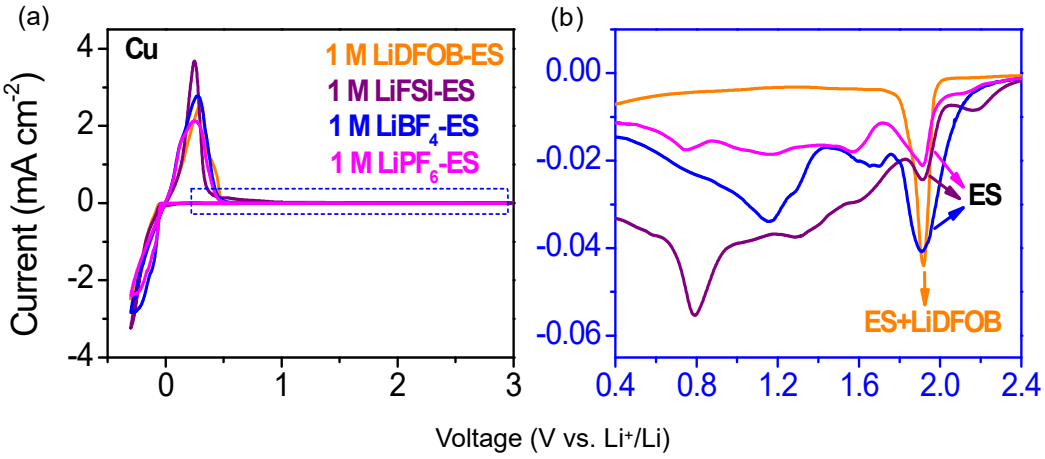

Fig. S1 CV curves of a Cu electrode in different electrolytes at a scanning rate of 0.2 mV s^{-1}. For the electrolytes of 1 M $LiBF_4$-ES, 1 M $LiPF_6$-ES and 1 M LiFSI-ES, a significant reduction current remained after the reduction decomposition of ES at 1.9 V, indicating that the ES-derived SEI alone is not compact enough.

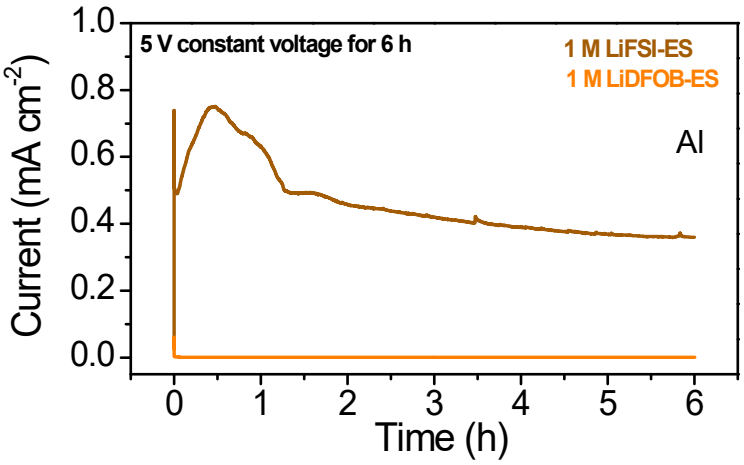

Fig. S2 The leakage current density dependent of time in a chronoamperometry test of an electrode at 5 V. The Al electrode suffered from severe anodic Al dissolution in 1 M LiFSI-ES electrolyte, whereas no anodic dissolution of Al occurred in 1 M LiDFOB-ES electrolyte.

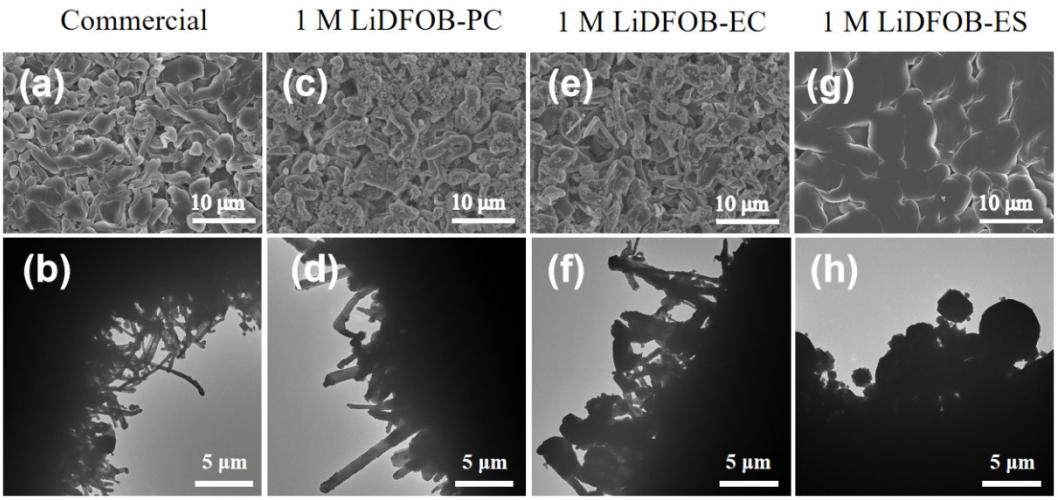

Fig. S3 SEM (a, c, e and g) and Cryo-EM (b, d, f and h) images of the morphology of lithium deposition in different electrolytes with a capacity of 0.25 mAh cm^{-2} at 0.5 mA cm^{-2}.

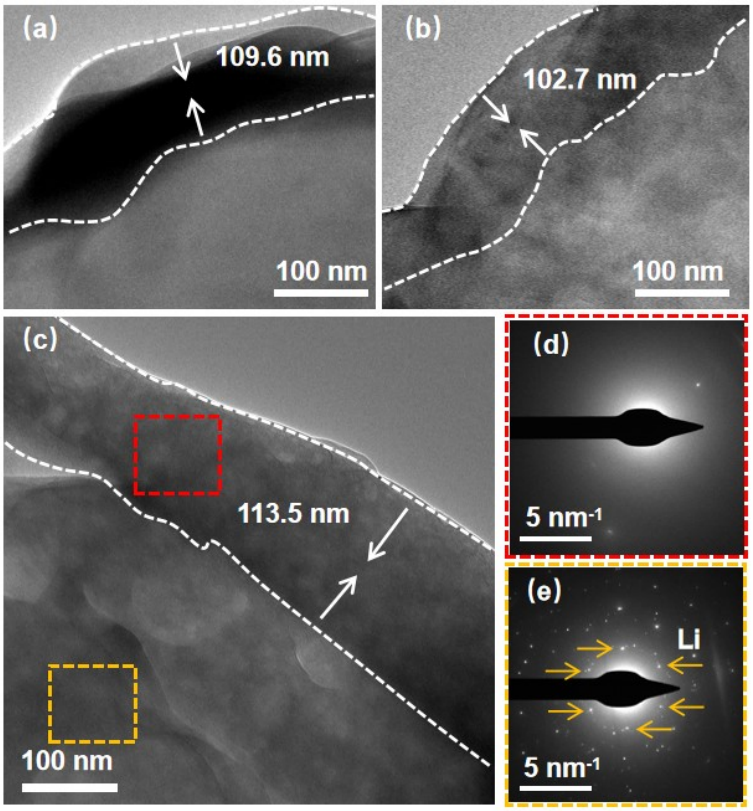

Fig. S4 (a-c) Cryo-EM images of SEI on the Li metal after 50 cycles in 1 M LiDFOB-PC electrolyte. (d, e) Electron diffraction images of the selected region in (c): d, red square; e, yellow square.

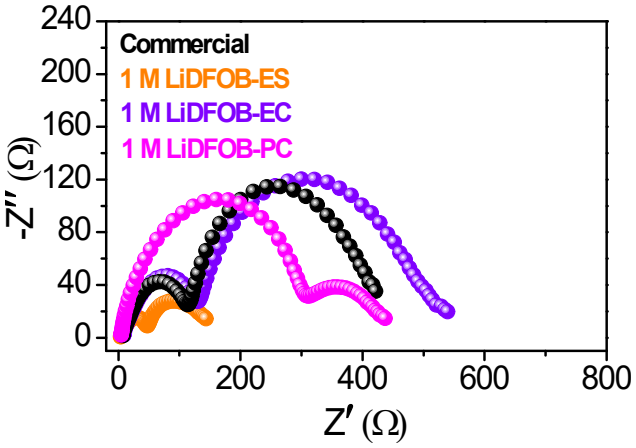

Fig. S5 Electrochemical impedance spectra of Li||Li symmetric cells using different electrolytes after 50 cycles.

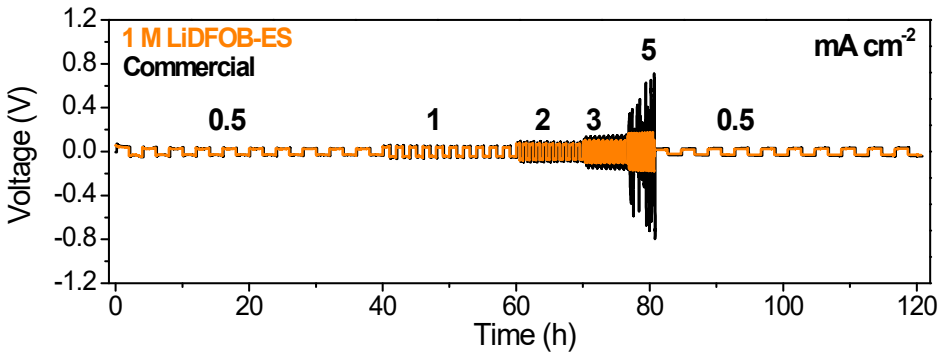

Fig. S6 Rate profile for Li||Li symmetric cells using 1 M LiDFOB-ES and commercial (1 M $LiPF_6$/EC:DMC (1:1 by vol.)) electrolyte. Li||Li cells at current density from 0.5 to 5 C, 1 C=1 mA cm^{-2}.

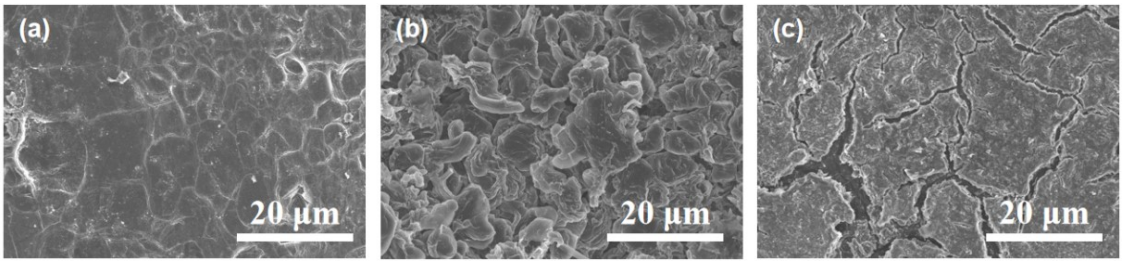

Fig. S7 SEM images of the morphologies of the Li metal anode harvested from the Li||Li symmetric cells after 50 cycles in (a) 1 M LiDFOB-ES, (b) 1 M LiDFOB-EC,(c) 1 M LiDFOB-PC electrolytes.

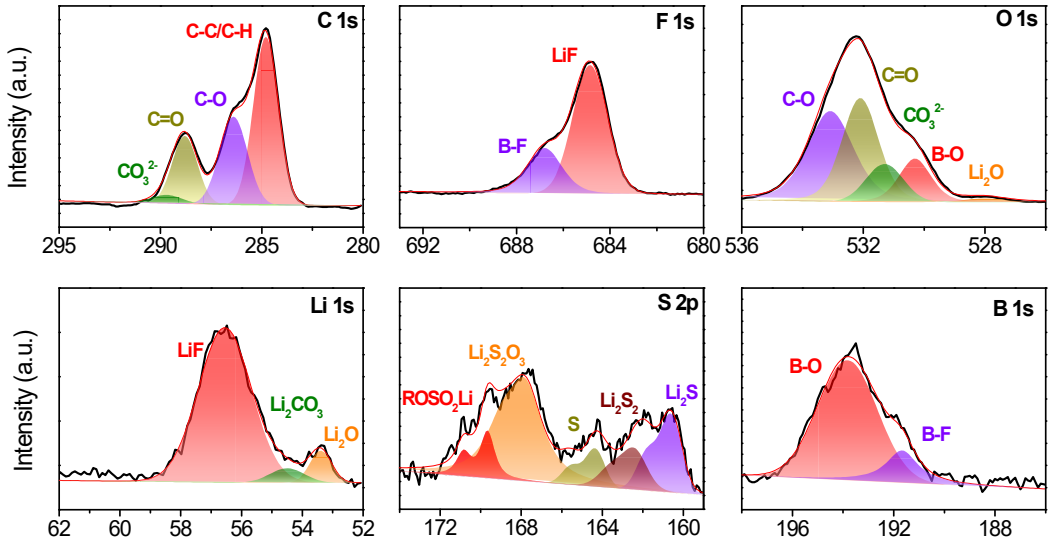

Fig. S8 XPS spectra of Li metal anodes after 100 cycles in 1 M LiDFOB-ES electrolyte.

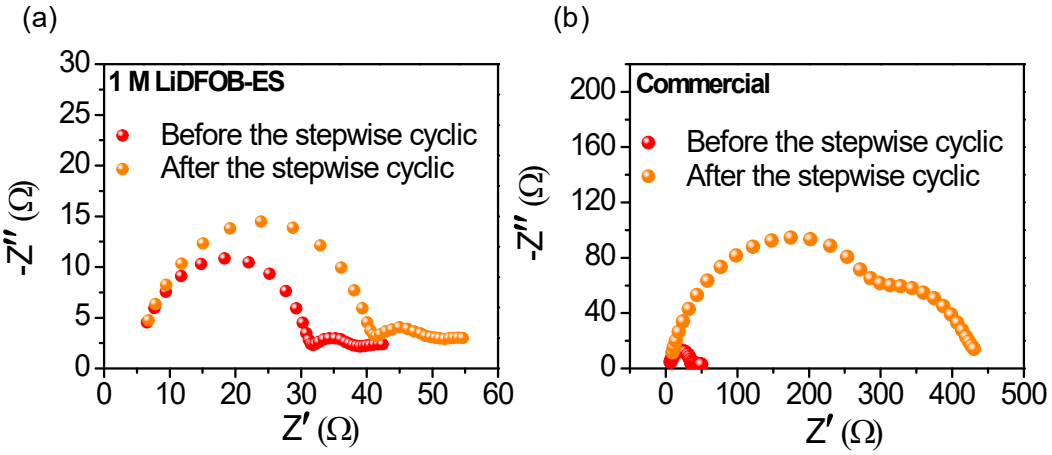

Fig. S9 Electrochemical impedance spectra of NCM622||Li half-cells before and after voltage-stepwise cycling from 4.3 V to 4.7 V in (a) 1 M LiDFOB-ES and (b) Commercial electrolytes.

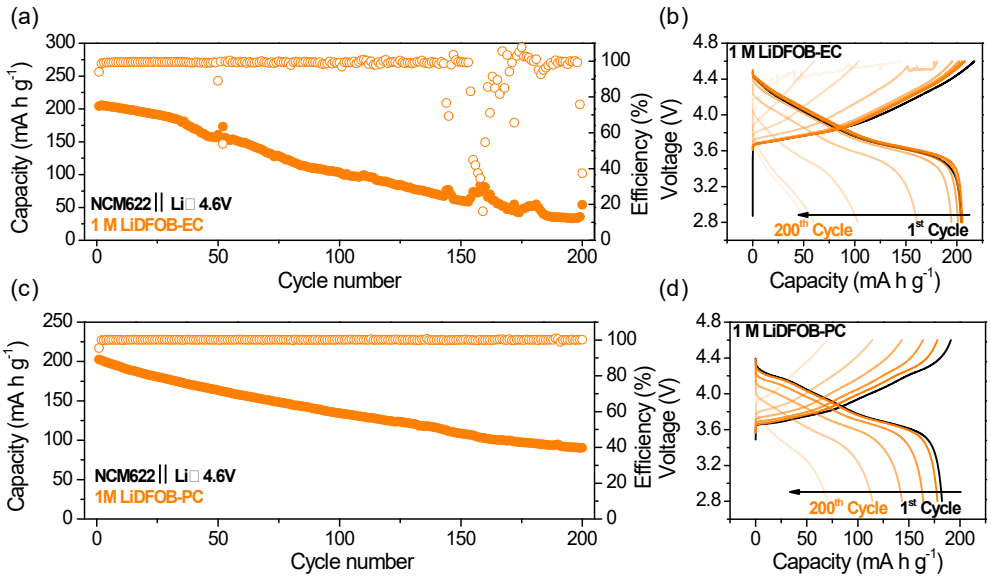

Fig. S10 Cycling performance and voltage profiles of the NCM622||Li half-cells using (a, b) 1 M LiDFOB-EC and (c, d) 1 M LiDFOB-PC.

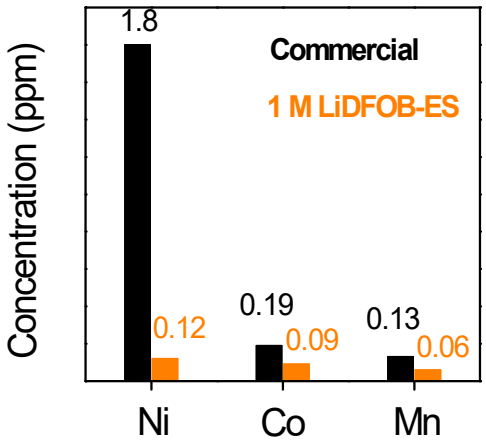

Fig. S11 Transition metal dissolution measured by ICP-MS after 400 cycles in 1 M LiDFOB-ES and Commercial electrolytes.

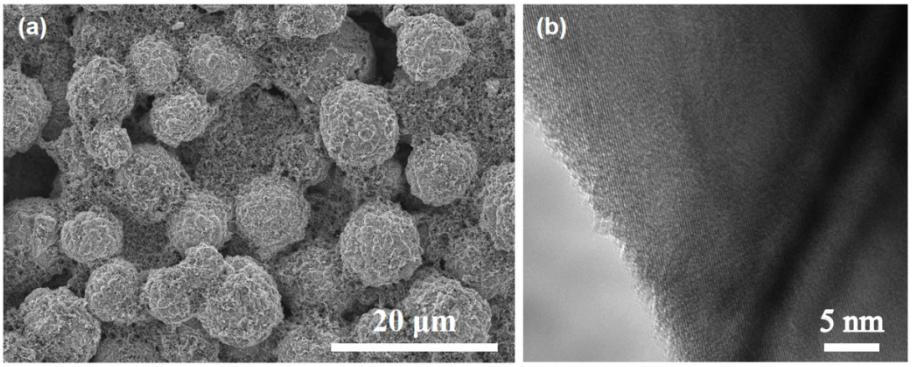

Fig. S12 (a) SEM and (b) TEM images of Pristine NCM622 particles.

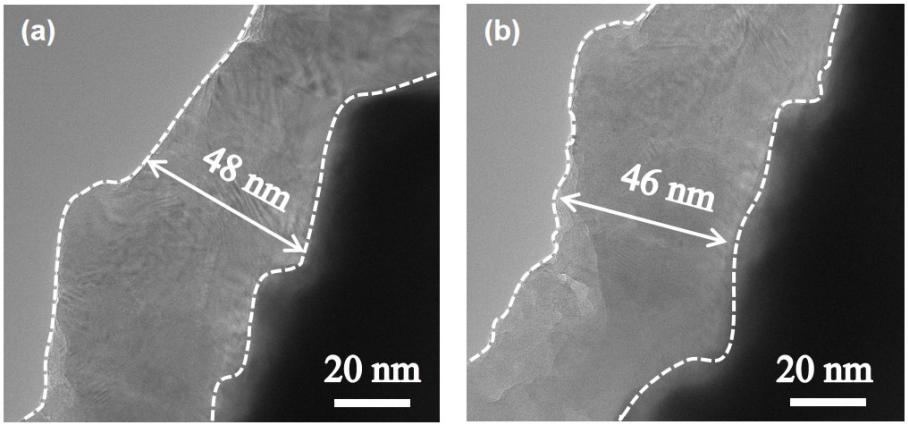

Fig. S13 TEM image of NCM622 electrode after 100 cycles in (a) 1 M LiDFOB-EC electrolyte and (b) 1 M LiDFOB-PC electrolytes.

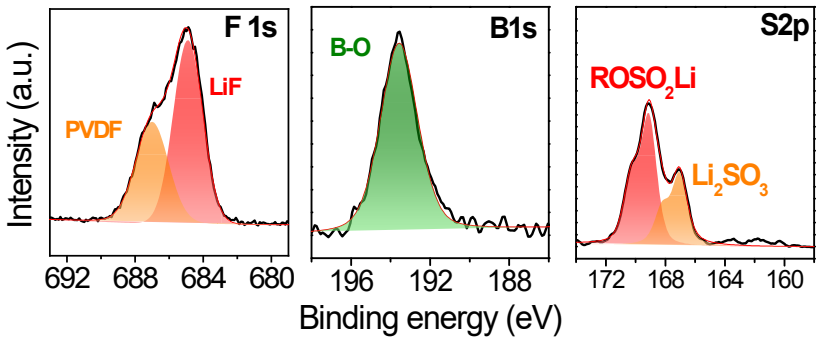

Fig. S14 XPS chemical analysis of CEI layers for the cycled NMC622 in 1 M LiDFOB-ES electrolytes.

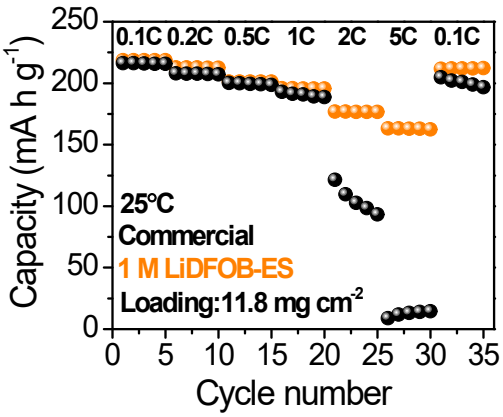

Fig. S15 Rate performance of NMC622||Li full-cells using 1 M LiDFOB-ES and commercial electrolytes at 25 °C.

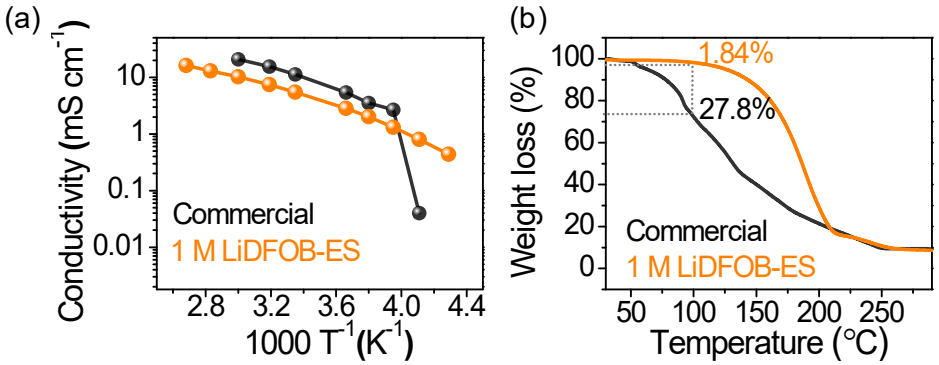

Fig. S16 (a) Ionic conductivities and (b) TGA curves of the 1 M LiDFOB-ES and commercial electrolytes.

Table S1. Ionic conductivities of 1 M LiDFOB-ES and commercial electrolytes at different temperatures

Electrolytes	Ionic conductivities (mS cm^{-1})										
	-50 ℃	-40 ℃	-30 ℃	-20 ℃	-10 ℃	0 ℃	25 ℃	40 ℃	60 ℃	80 ℃	100 ℃
1 M LiDFOB-ES	0.032	0.44	0.8	1.31	2.01	2.83	5.47	7.38	10.21	12.94	16.11
Commercial	-	-	0.04	2.87	4.5	6.42	12	18	20	*	*

* These values were underestimated because a significant amount of electrolyte was ejected from the cell by the accumulated pressure inside the cell at elevated temperatures.

Table S2. Comparison of our work with prior work on high-voltage NMC||Li batteries

Electrolyte		Cell parameters			Battery performance		
Electrolyte	**Ionic conductivity (mS cm^{-1})**	**Cathode/ anode**	**Cathode loading (mAh cm^{-2})**	**N/P ratio**	**Cycle stability (25 ℃)**	**Rate performance (25 ℃)**	**Test temperature**
1 M LiDFOB-ES (Our work)	25 ℃：5.47 -40 ℃：0.44	NCM622/ Li	2.5	4	4.6 V, 0.5 C : 88.2% (200 cycles), 92% (100 cycles)	0.1 C: 218.6 mA h g^{-1} 5 C: 163.3 mA h g^{-1}	-30-60 ℃
LiFSI-1.2DME-3TTE. Ref: [1]	25 ℃：2.44	NCM811/ Li	4.2	2.38	4.4 V, 0.33 C: >80% (150 cycles)	0.1 C: 210 mA h g^{-1} 6 C: 110 mA h g^{-1}	25 ℃
1 m LiFSI-DMTMSA. Ref: [2]	30 ℃：1.37	NCM811/ Li	4	0.39	4.7 V, 0.5 C : 88.1% (100 cycles)	0.1 C: 231 mA h g^{-1} 2 C: 186 mA h g^{-1}	25 ℃
1 M LiFSI-DME-TFEO. Ref: [3]	25 ℃：1.1	NCM811/ Li	1.5	5.9	4.4 V, 0.33 C : 80% (300 cycles)	0.1 C: 231 mA h g^{-1} 4 C: 137 mA h g^{-1}	25-55 ℃
LiFSI-1.5DMC-1.5TTE. Ref: [4]	25 ℃：1.7	NCM622/ Li	1.5	half-cell	4.6 V, 2 C : 80.1% (200 cycles)	0.2 C: 204 mA h g^{-1} 5 C: 125 mA h g^{-1}	25-60 ℃
10 M LiFSI-EC-DMC. Ref: [5]	-	NCM622/ Li	2.5	half-cell	4.6 V, 0.1 C : 86% (100cycles)	0.1 C: 225 mA h g^{-1}	25 ℃
0.6 M LiTFSI+0.4 M LiBOB+0.05$LiPF_6$-EC-EMC. Ref: [6]	-	$LiNi_{0.76}Mn_{0.14}Co_{0.1}O_2$/Li	0.9	half-cell	4.5 V, 0.33 C : 90% (200cycles)	0.1 C: 220 mA h g^{-1} 5 C: 129 mA h g^{-1}	30 ℃
1 M $LiPF_6$-FEC-FEMC. Ref: [7]	20 ℃：0.2	NCM523/ Li	1.75	half-cell	4.7 V, 0.2 C : 81% (200 cycles)	0.2 C: 190 mA h g^{-1} 2 C: 100 mA h g^{-1}	25 ℃
1 M $LiPF_6$-EC-DEC-EMC-10wt% FEC. Ref: [8]	-	NCM622/ Li	-	half-cell	4.6 V, 1 C : 87.3% (100 cycles)	0.2 C: 222 mA h g^{-1} 5 C: 140 mA h g^{-1}	25 ℃
1 M $LiBF_4$-FEC-SN. Ref: [9]	-	NCM523/ Li	-	half-cell	4.7 V, 0.5 C : 73.6% (100 cycles)	0.5 C: 185 mA h g^{-1} 5 C: 90 mA h g^{-1}	25 ℃
8.67 m $LiBF_4$-DMC. Ref: [10]	-	NCM523/ Li	-	half-cell	4.6 V, 0.1 C : 92.2% (50 cycles)	0.1 C: 200 mA h g^{-1} 5 C: 90 mA h g^{-1}	25 ℃

Note: The mark “-” means the corresponding information was not provided in the literatures.

M: mol L^{-1}; m: mol kg^{-1}.

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